PROPERTIES OF NON-STOICHIOMETRIC METALLIC CARBIDES

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AMR — ADVANCED METALS RESEARCH CORPORATION

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SOMERVILLE 45, MASS.

CONTRACT NO. NASw-663

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National Aeronautics and Space Administration
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Properties of Non-Stoichiometric Metallic Carbides

I. Objectives of Work During Quarter

A. Preparing stocks of powders of TiC of non-stoichiometric composition suitable for property measurements.

B. Density measurements on powders over the composition range of TiC.

C. Examination of a single crystal specimen of TiC.

D. Resistivity and Hall coefficient measurements on single crystals of TiC.

II. Preparation of Powder Specimens

Stock powder specimens in the TiC system have been prepared over the C/Ti mole ratio range of 0.60 to 0.95 for use in property measurement. The technique employed in preparing these specimens was essentially that described in previous reports. Two methods were employed. At compositions of $TiC_{0.80}$ and above, the hydride and graphite mixtures were placed in open graphite crucibles and heated in high vacuum at 1950°C for 3 hours. Experience has shown that under these conditions the oxygen content can be maintained at something less than 0.1% by weight.

The use of such high temperatures is not suitable for the lower C/Ti ratios because the titanium loss is so great that regardless of the starting compositions, ratios of less than about 0.75 cannot be maintained in the final sample. Consequently, lower temperatures, of the order of 1650°C must be employed and to obtain good reaction of the reduced hydride and graphite, the powders must be compacted. Analysis has shown that specimens prepared at this temperature invariably contain oxygen in the range of 1 to 2 weight percent, regardless of the care used in preparation. As long as the powder metallurgy technique is employed this situation appears to be inevitable. In the stocks of powders prepared, those above about $TiC_{0.75}$ are relatively low in oxygen while those below are relatively high in this element. It is believed that only by melting in an inert atmosphere and carrying to very high temperatures can low oxygen specimens be obtained in the low carbon range.

Each batch of carbide has been analyzed chemically for carbon content and precise measurement of lattice constant made. The specimens fall very closely on the lattice parameter composition curve previously reported.

III. Precision Density Measurements

Density measurements were made on TiC powder specimens over the range of carbon composition. The method used employed a pycnometer which consisted of a one milliliter vial, a stopper

having a capillary opening and a cap to prevent liquid loss during weighing.

The measurements were carried out in the following steps:

1. The TiC powder was crushed and sieved to -100 + 400 mesh.
2. The pycnometer was weighed empty and then with a specified amount of powder.
3. The open vial of powder was placed in a vacuum enclosure and pumped down while being vibrated.
4. Low vapor pressure oil previously outgassed was heated and introduced into the vial containing the powder while still under vacuum.
5. After cooling, the enclosure was opened to atmosphere, the vial removed and transferred to a constant temperature thermostat.
6. The vial and contents were brought to 23°C, stoppered, tipped off and capped.
7. After carefully freeing the outside of all oil and water the pycnometer and contents were weighed.

The above steps were repeated at the end of each run using the same batch of oil but with no specimen in the pycnometer in order to determine the oil density precisely.

The volume of the pycnometer was calibrated using solid bars of silicon of known density. The entire procedure was repeated with powdered silicon sieved to -100 + 400 mesh. The difference in the volume obtained by the two procedures was

less than 0.5% which is estimated as the reproducibility of the density measurements.

The x-ray density was determined using the measured lattice parameters according to the formula

$$D_{x\text{-}ray} = 1.6602 \frac{4(47.90 + 12.01\chi)}{a_o^3}$$ which assumes no vacancies

in the metal atom sites in the unit cell. χ is the C/Ti mole ratio. Table I lists the C/Ti ratio, lattice parameter, x-ray density and pycnometer measured density for a series of TiC powder specimens. A plot of these values is shown in Fig. 1. The closed circles represent the x-ray density and the open circles the measured density. The continuous curve shown is the x-ray density calculated directly from the continuous curve of lattice parameter vs C/Ti ratio determined in earlier work[1] and reproduced as Fig. 2. The accuracy of the x-ray density measurements was about 0.1%. The reproducibility of the pycnometer measured density was on the average about 0.5%. In the plot of Fig. 1 it is seen that the agreement of the pycnometer measured density with the x-ray density is well within experimental error for all of the points except No. 7 and No. 9. The latter value was obtained on a commercial and impure carbide. A one percent decrease in the pycnometer density from the x-ray density represents a vacancy concentration of one in four hundred in the metal atom sites.

It is interesting to note that the peak in the lattice parameter vs C/Ti ratio curve is not reflected as an anomaly

in the density curve. The fact that there is no significant deviation between the pycnometer measured density and the x-ray density in the vicinity of the peak in lattice parameter indicates that all of the metal atom sites are occupied over the whole composition range and that carbon sites are occupied up to the limit determined by the carbon content, the remainder of the sites being vacant. It is not possible then to describe the peak in the lattice parameter curve as resulting from the presence of vacant metal atom sites and one must conclude that the peak is a reflection of the changing bond length with carbon content and not to any anomalous distribution of atoms on atom sites. It seems strange that the maximum bond length should occur at the position of maximum stability as indicated by the melting point maximum which occurs at approximately the same composition as the lattice constant maximum but the experiments carried out thus far indicate that this is the case. A similar situation is to be found in the Zr-C system and no obvious explanation presents itself. This is an important matter for further consideration.

IV. Examination of a Single Crystal Specimen of TiC

Since it had not been possible to prepare, by powder metallurgy techniques, a dense single crystal specimen of the carbides, a specimen of single crystal TiC was obtained through the kindness of a colleague at M.I.T. in order to

gain some experience in specimen preparation and property measurement on this kind of material.

The full history of the specimen about 2 inches long and 3/8 inch diameter was not known. A chemical analysis showed the average composition to be $TiC_{0.94}$ and the lattice constant was measured as 4.3298 Å which places it closely on the previously determined lattice parameter composition curve.

Metallographic examination showed that the crystal was free from porosity and there was no evidence of the presence of a second phase. The orientation of the specimen was determined by x-rays and attempts were made to cleave the specimen on the cube planes. The cleavage was partially successful, areas in the center of the cylindrical specimen cleaving readily on the cube planes but the fracture near the outer surface was irregular suggesting the presence of high residual stresses in the crystal as grown. Sawn sections sometimes showed cracks parallel to the cube directions also indicative of high residual stresses.

Another significant feature of the cleavage was the fact that cleaved faces sometimes showed a small but localized change in direction indicative of a small angle grain boundary with a misorientation of 2 to 3 degrees. There were relatively few of these boundaries but they showed clearly on the cleaved surfaces and could be followed for some distance through the crystal.

Resistivity measurements suggested the possibility of carbon content variations in the crystal, possibly between the center and surface. Since no method of quantitatively determining the carbon content at a particular point is presently available it seemed worthwhile to examine the variations in the titanium content by means of the electron beam microanalyzer. In this technique, the intensity of the titanium characteristic x-radiation from a one micron spot on the specimen is compared directly with that from a reference standard of pure titanium. Although the results did not constitute a detailed survey because of the limited material available, they indicated definite variations in the titanium content from center to surface and along the length of the specimen of as much as 5 to 6 weight percent. With present calibration techniques the absolute value of the titanium content cannot be fixed closer than about 2 weight percent but the point to point variations of at least 1 weight percent can certainly be detected on smooth flat specimens.

This possibility of composition variation within the single crystal makes it imperative that some method of analysis be available to check the individual specimens upon which electrical and mechanical properties are to be measured.

V. Resistivity and Hall Coefficient Measurements

It was found that the cleavage of the crystal was not sufficiently dependable to produce regular rectangular specimens for measurement so the crystal was cut into thin slices

parallel to the cube planes with a diamond saw and these slices further cut into rectangular plates or bars approximately 0.5mm x 2mm x 10mm. Some of the plates were cut with an ultrasonic tool into the form of bridge specimens with integral potential contacts such as used in semiconductor work. Such a bridge is shown in Fig. 4. Preparation of these specimens emphasized the extreme fragility of the material, it being much more difficult to handle than, for instance, silicon or germanium.

The problem of making satisfactory electrical contacts with the specimens has not been solved in a satisfactory fashion, particularly in view of the desirability of making measurements above room temperature. Ultrasonic soldering almost invariably resulted in fracture of the specimen in the vicinity of the joint. Conductive paints of various kinds gave erratic results especially when the temperature of the specimen was changed. So far, pressure contacts have given the best results but are far from satisfactory. Experiments are underway on techniques for electroplated contacts which it is hoped will overcome this difficulty and permit the use of the bridge type specimens.

Room temperature resistivity measurements were made on two bars using a fixture essentially as shown in Fig. 3. Current contacts were made by pressure applied through thin copper foils at the ends of the specimen. Potential contacts

were steel needle points pressed against the top face of the specimen. The whole unit was placed in a constant temperature bath. Several values of current were used and the current reversed to minimize thermoelectric effects. The results are shown below:

Specimen	Temperature	Resistivity, microhm cm.
A	23°C	180 ± 5
B	23°C	160 ± 5

Specimen B was measured over a range of temperatures in a thermostat with the results shown in Fig. 5 plotted as the ratio ρ/ρ_o where ρ_o is the resistivity at 23°C. The scatter in the experimental points is due to the unsatisfactory nature of the current contacts at the ends of the specimen so that it was difficult to maintain a constant current for any length of time.

The curve is generally linear with a positive slope. The resistivity is lower and the temperature coefficient of resistivity somewhat higher than reported by Hollander[2].

Attempts to measure the Hall coefficient of the TiC crystal have so far been unsuccessful. Using experimental conditions which have proved very satisfactory for low resistance silicon and other semiconductors, the Hall voltage on the TiC proved too small for detection with presently available instruments. Part of the difficulty is the contact problem but at the same

time the results indicate that the Hall coefficient is quite small, of the order of that of normal metals and consequently the carrier concentration is high as would be expected if the conduction mechanism is of the normal metallic type. This is in line with the resistivity and its temperature coefficient. In order to obtain significant values of the Hall coefficient, a more sophisticated experimental technique such as used for normal metals will be required, including reliable contacts, much higher current densities and higher magnetic fields.

Perhaps the most significant finding of the present experiments is the suggestion of a significant compositional variation within the individual single crystal specimens. This is a problem which will require critical examination and it will really be necessary to test each specimen cut from the crystal. Unfortunately, the lattice constant is not a reliable index in the particular region of interest. Progress is being made at AMR in the quantitative determination of carbon with the electron beam microanalyzer but present techniques do not have the precision required. Perhaps the resistivity will prove to be the sensitive indicator required, provided enough crystals become available to establish the necessary relationships.

VI. Plans for Continuation of Work

Work will continue on those properties which are measurable on powder specimens. These include:

A. Thermal expansion measurements using x-ray high temperature camera up to temperatures of about 1000°C.

B. Thermoelectric power measurements over a range of temperature on specimens of pressed powder.

C. Magnetic susceptability measurements on powder samples using well established techniques.

References:

1. Norton, J. T. and Lewis, R.K., NASA Contract No. NASr-98 (1963).

2. Hollander, L. E., J. Appl. Phys. 32, 996 (1961).

TABLE I

TiC Specimens for Density Measurements

Specimen No.	C/Ti	a_o	$D_{x\text{-ray}}$ (gm/cm^3)	$D_{pyc}^{23°C}$
1 - T24A	0.614	4.3144	4.57	4.60
2 - T24A	0.654	4.3185	4.60	4.55
3 - T27B	0.818	4.3319	4.72	4.70
4 - T27B	0.821	4.327	4.72	4.66
5 - T24B	0.835	4.3305	4.75	4.75
6 - T22H	0.861	4.3307	4.76	4.78
7 - T27B	0.856	4.3303	4.76	4.66
8 - T27B	0.912	4.3308	4.82	4.86
9 - T K	0.940	4.3268	4.85	4.90
10 - T L	0.942	4.3298	4.84	4.83

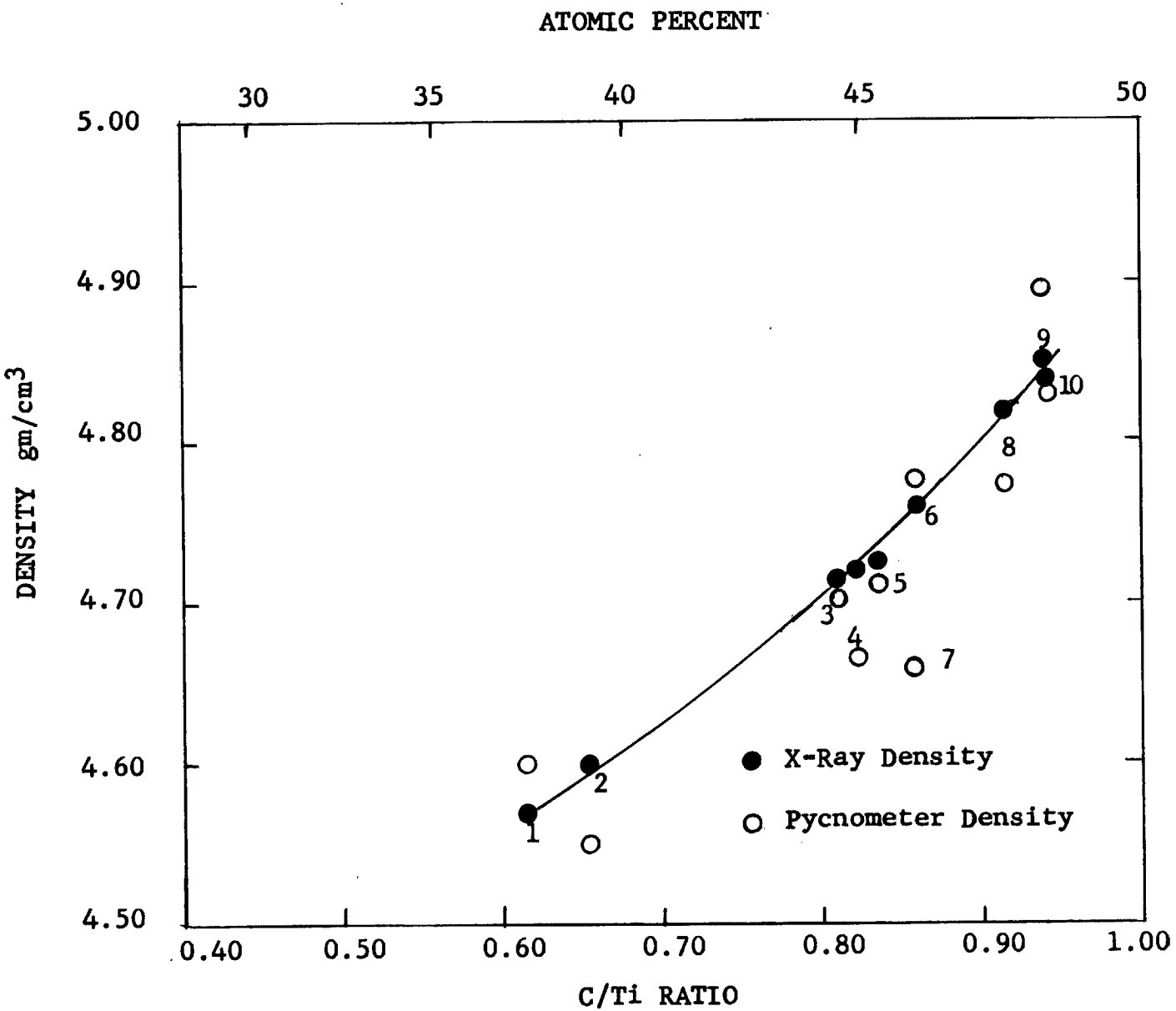

FIG. 1 TiC DENSITY VS COMPOSITION

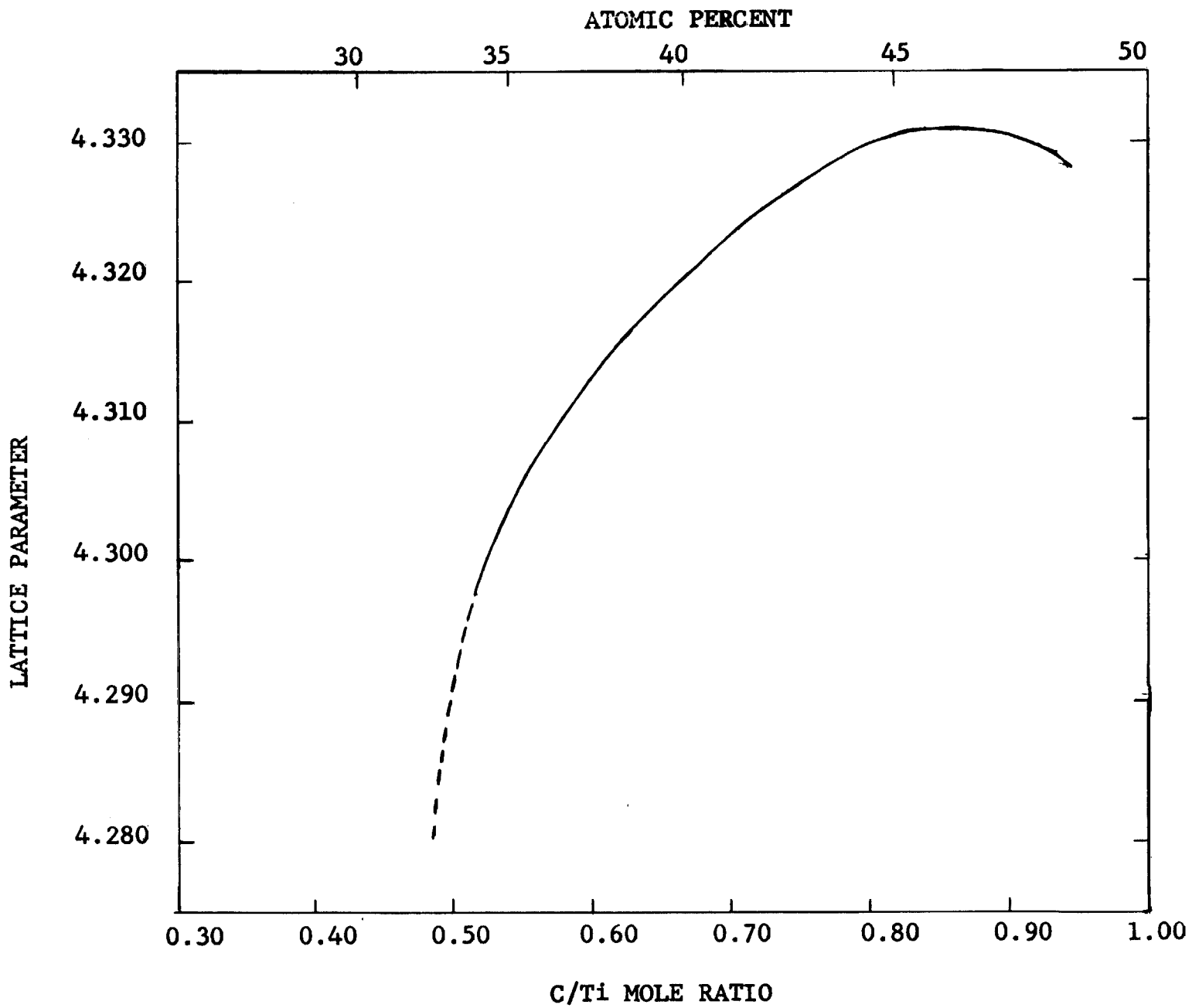

FIG. 2 TiC LATTICE PARAMETER VS. CARBON COMPOSITION

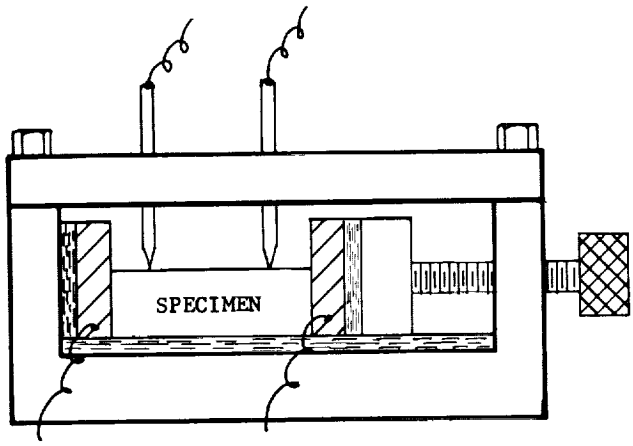

FIG. 3 RESISTIVITY SPECIMEN HOLDER

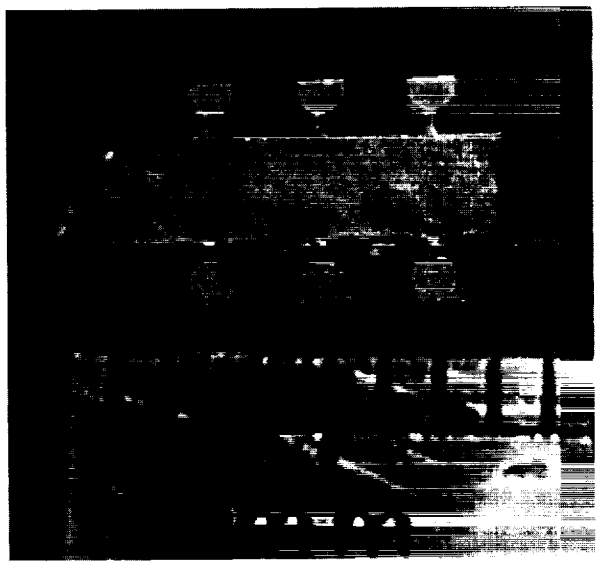

FIG. 4 BRIDGE SPECIMEN

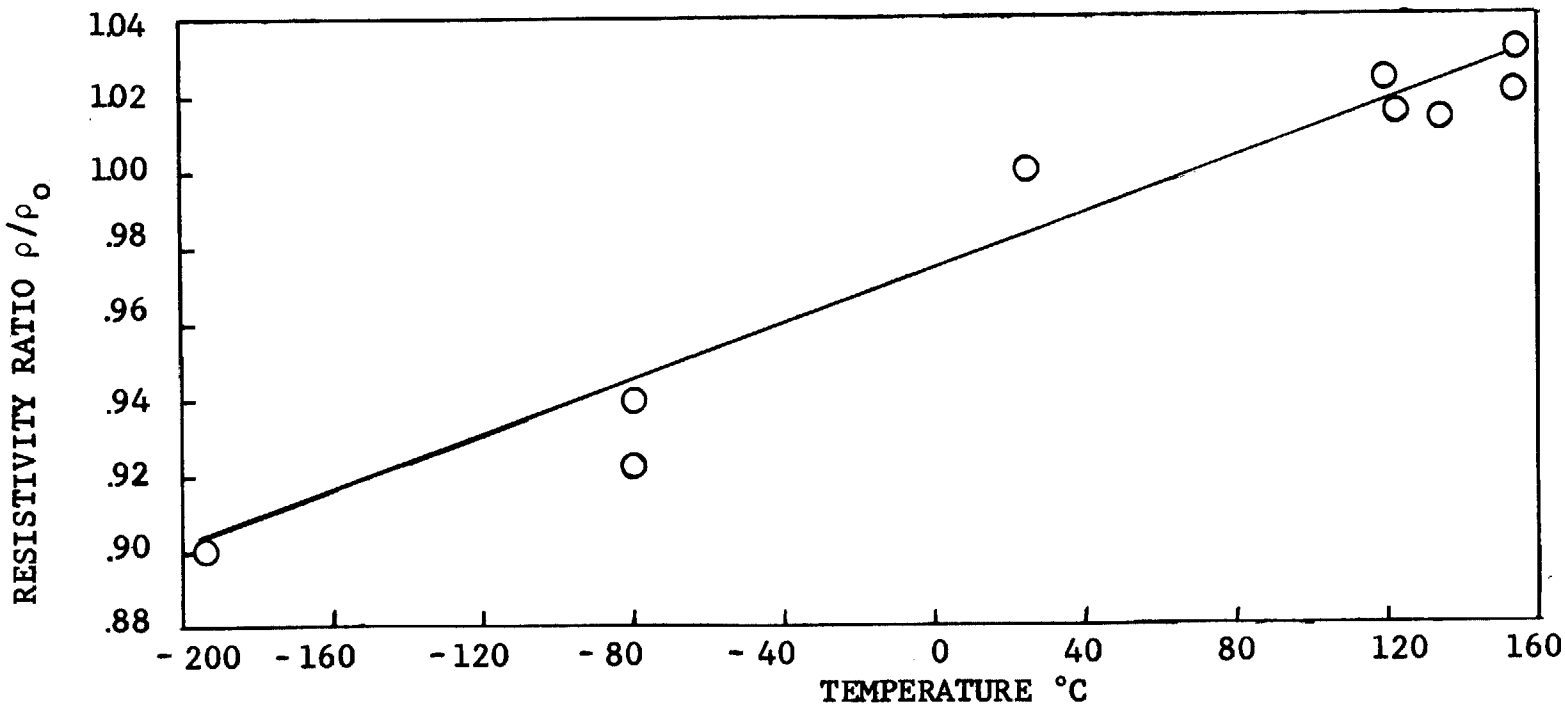

FIG. 5 RESISTIVITY RATIO ρ/ρ_o VS TEMPERATURE